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TITLE: LAMINATE FOR CONTAINER AND PAPER CONTAINER FOR LIQUID CONTENT MANUFACTURED THEREFROM

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I, the below named translator, hereby declare that:

My name and post office address are as stated below:

That I am knowledgeable in the English language and the Japanese language and that I believe the English translation of the specification, claims and abstract relating to the above application is a true and complete translation.

I hereby declare that all statements and herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 101 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: July 8, 2004

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DESCRIPTION

LAMINATE FOR CONTAINER AND PAPER CONTAINER FOR LIQUID CONTENT MANUFACTURED THEREFROM

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a lamination product and a carton using thereof, particularly to a lamination product which possesses a good barrier property of interrupting the penetration of oxygen gas or water vapor, which is free of pin-hole defect, which is capable of avoiding a poor seal and liquid leak events, and preventing content from deteriorating, and which also holds superiority in preservation, storage, or the like, and a carton using thereof.

Related Arts

Hitherto, various types of cartons for liquid has been developed and proposed which packs liquors, juices or soft drinks, mineral water, liquid seasonings, or other liquid foods and drinks.

With respect to the packaging material for composing such a carton for liquid, it is particularly preferable to have a good barrier property of interrupting the penetration of oxygen gas or water vapor, and a good moisture-proofness. Thus, the most important thing for lamination product used as the packaging material is the selection of a barrier material to be a part of the lamination product.

As the barrier material, for example, metallic materials such as aluminum foil or aluminum evaporating film; resinous material such as poly vinylidene chloride or ethylene-vinyl alcohol copolymers, and transparent barrier films prepared by evaporating an inorganic oxide such as silicon oxide or aluminum oxide as a film onto a face of base film such as biaxial oriented nylon film, which comes into focus, are known.

The barrier material have to be processed, for example, by laminating at least in the order of a polyolefin type resin layer (heat-sealing resin layer) / paper base / adhesive resin layer / barrier material / polyolefin type resin layer (heat-sealing resin layer) in order to prepare a lamination product. Subsequently, the lamination product is subjected to creasing ruled lines, while punching into a blank having a predetermined figure. Then, in order to prevent penetration and leaks of contents, end-face processing, such as, skive hemming processing, etc., is performed to the end face of the blank, and which will be followed by frame processing or hot-air processing at the seal section in order to perform the body part sealing by frame seal or hot-air seal, thus, a tubular sleeve being manufactured.

Next, the tubular sleeve thus manufactured is delivered to the food manufacturer, etc., where the contents to be packed is filled up, and the tubular sleeve is supplied to a contents filling machine. On the filling machine, in advance of the content filling, the inner surface of the bottom of the sleeve

is heated by hot-air or the like, and which is followed by press sealing in order to give a sealed bottom. After that, the bottomed sleeve is filled with the contents. Further, the inner surface of the top of the bottomed is heated by hot-air, which is followed by press sealing in order to give a sealed top, thus, the sealed carton for liquid which is filled with contents being obtained.

When the metallic material such as aluminum foil is used as the barrier material in the lamination product which consists of the above specifications, it can bring an outstanding barrier property as well as a good light-tight property, and thus it is very useful. However, since the metallic foil such as aluminum foil has a poor flexibility, the lamination product used such metallic foil tends to cause the pin-hole defect, and which will end in a remarkable deterioration of the barrier property. Further, when the used carton is disposed, the metal such as aluminum included in the carton will remains as-is after incineration. The metal waste may damage the incinerator used. Thus, with respect to the lamination product used such metallic foil, the lack of incineration aptitude, as well as the lack of environmental aptitude, which may cause the environmental destruction, will arise.

When the resinous material such as poly vinylidene chloride is used as the barrier material, an effectiveness in a satisfactory degree can be expected for the gas barrier property which prevents penetration of oxygen gas, water vapor,

etc. However, since such material includes chlorine ingredient, toxic gases, such as dioxin, etc., will be generated when the used carton is disposed by incineration. As is generally known, there are concerns that such gases adversely affect human body or others. Therefore, the lack of incineration aptitude, as well as the lack of environmental aptitude, which may cause the environmental destruction, will arise for the lamination product used such chlorinate resin, as is the case with the metallic foil.

When the resinous material such as ethylene-vinyl alcohol copolymer is used as the barrier material, an effectiveness in a satisfactory degree can be expected, under the absolute dry condition, for the gas barrier property which prevents penetration of oxygen gas, water vapor, etc. However, under wet condition, its gas barrier property comes into a remarkable low degree, and the product would never be fit for practical use.

When the transparent barrier film prepared by evaporating an inorganic oxide such as silicon oxide or aluminum oxide as a film onto a face of base film such as biaxial oriented polyethylene terephthalate film or biaxial oriented nylon film is used as the barrier material, a problem will arise that defects such as crack in the vapor deposited film of inorganic oxide are easily brought on by external forces, such as heat or pressure. Because, the vapor deposited film of inorganic oxide such as silicon oxide or aluminum oxide is a glassy, inelastic, thin film which possesses a

poor flexibility. Once the crack occurs on the vacuum evaporated film of the inorganic oxide, comes into a remarkable low degree, and the product would never be fit for practical use. For example, when a paper base and the transparent barrier film mentioned above which faces each other so that the vapor deposited inorganic oxide film side of the transparent barrier film is encountered to the paper is laminated via an anchor coat agent layer, for example, via a low density polyethylene resin which is heated at about 330°C and melt extruded between the paper and the barrier film from an extruder, the defect such as crack in the vacuum evaporated film of inorganic oxide are easily caused by the heated temperature of the melt extruded resin, and which results in the remarkable deterioration of the gas barrier property which prevents penetration of oxygen gas, water vapor, etc.

Moreover, with respect to the above carton for liquids, in the case that the lamination product which is prepared by laminating at least a polyolefin type resin layer (heat-sealing resin layer) /a paper base /an adhesive resin layer /a base film provided with a vapor deposited inorganic oxide film /a polyolefin type resin layer (heat-sealing resin layer) in this order is used, and the hot-air is blown to the inner surface of the lamination product in order to form the tubular sleeve, bottom part, or top part, a low density polyethylene resin is typically used as the polyolefin type resin layer (heat-sealing resin layer) which forms the inner

surface of the lamination product, and the heat-seal is usually performed at a temperature of about 320°C to 350°C. In such a situation, when the heat seal is performed at the temperature condition, a pin-hole caused by heat occurs exceedingly easily at the inside of the lamination product to be shaped into the carton. When the pin-hole occurs, problems such as poor sealing, liquid leak, are encountered, and which problems are accompanied with further problems such as deterioration of contents, poor preservation and poor storage stability. In some cases, the commercial value of the product falls remarkably, and discard has to be performed.

As the pin-hole occurred in carton, the known are the pin-hole caused by burr in ruled crease line which occurs at the time when the lamination product is subjected to creasing ruled lines, while punching into a blank having a predetermined figure; and the pin-hole caused by heat which occurs at the time when the top or bottom of the tubular sleeve is heated by hot-air in order to fill the content, and the like.

The pin-hole caused by heat will be described in detail including the occurrence process thereof. As mentioned above, on the occasion of manufacturing the carton, in order to form the top section or the bottom section, a hot-air will be blown to the inner surface of the tubular sleeve at the top section or bottom section, from the diffuser of a heating chamber.

Here, although the hot air blown to the inner surface at the top or bottom of a tubular sleeve can fuse the heat-sealing resin which constitutes the heat-sealing resin

layer which forms the inner surface, the heat of hot-air happens to reach to a paper base, and thus the paper base is heated. When the paper base is heated, the moisture involved in the paper base is heated, and this tends to serve as a steam to be going to escape from the paper base to the inside or outside side surface of lamination product. Furthermore, by this event, resin films which were laminated in the lamination product are forced to migrate outwardly so as to swell, that is the blister phenomenon. When the heat by the hot air is further conducted to the resin films, the resin films located at the inner surface side and superposed on the paper can, no longer, sustain the steam pressure created by the water vaporization. Thus, the swelled resin films come into break, and that may be the emergence mechanism of pin-hole caused by heat. When observing the generation of the pin-hole caused by heat, in the liquid carton which was box produced from a lamination product where the low density polyethylene resin layer, a paper base, an adhesive polyethylene resin layer, a biaxial orientated polyethylene terephthalate film provided with an inorganic oxide deposition film, low density polyethylene film, etc were layered in this order from the external side., the bulge or blister phenomenon is observed at first in the adhesive polyethylene resin layer, as mentioned above. Then, so as to follow the phenomenon in the adhesive polyethylene resin layer, the bulge or blister comes to the biaxial orientated polyethylene terephthalate film provided with an inorganic oxide deposition film, and further to the

low density polyethylene film. At last, it will be observed that the pin-hole by heat appears as a result of breaking the blister.

SUMMARY OF THE INVENTION

Therefore, the present invention aims to provide an improved lamination product for container and a liquid carton using thereof. This invention aims to provide a lamination product for container which is excellent in the barrier property capable of inhibiting penetration of oxygen gas, steam, etc., which avoids poor seal, liquid leak, etc., resulting from the appearance of pin-hole, and which further prevents deterioration of contents, and is excellent in the preservative property or keeping quality; and a liquid carton using thereof.

I, the inventor, have noted that the coating film which is made of a resin composition comprising a resin and an inorganic lamellar compound exhibits an outstanding barrier property capable of inhibiting penetration of oxygen gas, steam, etc., and also an outstanding dampproofing property, after making various studies for solving the technical problems in the carton for liquid. Thus, the inventor have prepared, at first, a lamination product which is comprised at least of an outermost layer, a paper base, a barrier layer which is comprised of a coating film made of a resin composition including the resin and the lamellar compound, and an innermost layer layered in this order. Then, the inventor subjects the lamination product to creasing ruled lines, while punching

into a blank having a predetermined figure. For the next step, in order to prevent penetration and leaks of contents, end-face processing, such as, skive hemming processing, etc., is performed to the end face of the blank, and which will be followed by frame processing or hot-air processing at the seal section in order to perform the body part sealing by frame seal or hot-air seal, thus, a tubular sleeve being manufactured. Next, the tubular sleeve thus manufactured is supplied to a contents filling machine, where, in advance of the content filling, the inner surface of the bottom of the sleeve is heated by hot-air, and which is followed by press sealing in order to give a sealed bottom. After that, the bottomed sleeve is filled with the contents. Further, the inner surface of the top of the bottomed is heated by hot-air, which is followed by press sealing in order to give a sealed top, thus, the sealed carton for liquid which is filled with contents being obtained. Consequently, it has been found out that the carton for liquid can be obtained which prevents the occurrence of cracks or the like, and inhibits the appearance of pin-hole completely, thus, which is excellent in the barrier property capable of inhibiting penetration of oxygen gas, steam, etc., which avoids poor seal, liquid leak, etc., resulting from the appearance of pin-hole, and which further prevents deterioration of contents, and is excellent in the preservative property or keeping quality. As a result of these findings, the inventor has accomplished in the present invention.

That is, the present invention capable of solving the above mentioned problems is a lamination product which is comprised at least of an outermost layer, a paper base, the barrier layer which is made of coating film of a resin composition which is comprised of a resin and an inorganic lamellar compound, layered in this order.

Further, the present invention capable of solving the above mentioned problems is a carton for liquid which is characterized in that the carton is prepared by using the above mentioned lamination product, and subjecting the lamination product to box-forming.

By adopting such a constituent, the present invention can accomplish to manufacture the carton for liquid which is excellent in the barrier property capable of inhibiting penetration of oxygen gas, steam, etc., also in the dampproofing property, which completely inhibits the appearance of pin-hole by heat, or the like, further which avoids poor seal, liquid leak, etc., resulting from the appearance of pin-hole, and which further prevents deterioration of contents, and is excellent in the preservative property or keeping quality.

The present invention also provides a lamination product and a carton for liquid using thereof, wherein each layer of the inorganic lamellar compound has a size in the planar direction within the range of 3 to 5000 nm, in a state that the inorganic lamellar is subjected to completely delamination.

Further, the present invention provides a lamination product and a carton for liquid using thereof, wherein the thickness of each layer of the inorganic lamellar compound is not more than 10nm.

Further, the present invention provides a lamination product and a carton for liquid using thereof, wherein the aspect ratio of the inorganic lamellar compound is in the range of 30 to 50.

Further more, the present invention provides a lamination product and a carton for liquid using thereof, wherein the cation exchange capacity of the inorganic lamellar compound is not less than 30 meq / 100g.

Still more, the present invention provides a lamination product and a carton for liquid using thereof, wherein the layer surface of the inorganic lamellar compound has been chemical treated with an organic ammonium salt.

Further, the present invention provides a lamination product and a carton for liquid using thereof, wherein the inorganic lamellar compound is one or more of crayey minerals, preferably, includes at least lamellar silicate.

Further more, the present invention provides a lamination product and a carton for liquid using thereof, wherein the volume ratio of (inorganic lamellar compound / resin) is in the range of (5/95) to (40/60).

Still more, the present invention provides a lamination product and a carton for liquid using thereof, wherein the resin which is the constituent of the resin composition for

the barrier layer is comprised of a crystalline polyamide, or a blend of a crystalline polyamide and aliphatic polyamide, preferably, nylon MXD6 resin (N-MXD6) or a blend of N-MXD6 and an aliphatic polyamide.

Further, the present invention provides a lamination product and a carton for liquid using thereof, wherein the outermost layer is comprised of a polyolefin type resin having a heat-seal ability.

Further, the present invention provides a lamination product and a carton for liquid using thereof, wherein the paper base is that having a weighing in the range of 80 to 600 g/m^2.

Further, the present invention provides a lamination product and a carton for liquid using thereof, wherein the innermost layer is comprised of a polyolefin type resin having a heat-seal ability.

Furthermore, the present invention provides a lamination product and a carton for liquid using thereof, wherein the innermost layer is comprised of an ethylene - α-olefin copolymer polymerized with a metallocene catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic sectional view illustrating the layer construction of one example of the lamination product for liquid carton according to the present invention;

Fig. 2 is a schematic expansion plan view illustrating the configuration of the liquid carton in a step of the

box-producing process, which carton is manufactured by using the lamination product according to the present invention and is shown in Fig. 1;

Fig. 3 is a schematic perspective view illustrating the configuration of the liquid carton in another step of the box-producing process, which carton is manufactured by using the lamination product according to the present invention and is shown in Fig. 1;

Fig. 4 is a schematic perspective view illustrating the configuration of the liquid carton in further another step of the box-producing process, which carton is manufactured by using the lamination product according to the present invention and is shown in Fig. 1; and

Fig. 5 is a schematic perspective view illustrating the configuration of the liquid carton in still another step of the box-producing process, which carton is manufactured by using the lamination product according to the present invention and is shown in Fig. 1.

BEST MODE OF CARRYING OUT OF THE INVENTION

Now, the present invention will be described in detail with reference to the drawings. First, the construction of lamination product according to the present invention which will constitute the carton for liquid will be described by using an example illustrated in a drawing. Fig. 1 is a schematic sectional view illustrating the layer construction

of one example of the lamination product for liquid carton according to the present invention. Next, the construction of the carton for liquid according to the present invention will be described by using an example illustrated in drawings. Figs. 2, 3, 4 and 5 are a schematic expansion plan view and schematic perspective views each illustrating the configuration of the liquid carton in respective steps of the box-producing process, which carton is manufactured by using the lamination product according to the present invention and is shown in Fig. 1.

In the present invention, the lamination product A which constitutes the carton for liquid according to the present invention, as shown in Fig. 1, has a basic structure which is comprised at least of an outermost layer 1, a paper base 2, and a barrier layer 4 which consists of a coating film 3 made of a resin composition which is comprised of a resin and an inorganic lamellar composition, layered in this order. In this embodiment, an innermost layer 5 is further formed on another surface of the barrier layer 4, wherein the another surface is opposite to the surface to be contact with the paper base 2.

The above-mentioned instantiation is one embodiment of the lamination product which constitutes the carton for liquid according to the present invention, and the present invention is not limited thereto. For example, in the present invention, it is possible to design and manufacture various configurations of the lamination product, as the purpose of

packaging of the carton for liquid, the kind of contents to be packed, purpose of using, the uses of carton, etc., by layering any other substrates, although such modifications are not illustrated as drawings herein.

Concretely, various configurations, for example, (1) outermost layer / base material layer / barrier layer; (2) outermost layer / base material layer / barrier layer / innermost layer (above mentioned construction); (3) outermost layer / base material layer / adhesive resin layer / barrier layer / innermost layer; (4) outermost layer / base material layer / barrier layer / adhesive resin layer / innermost layer; (5) outermost layer / base material layer/ barrier layer / adhesive resin layer / thermoplastic resin layer / innermost layer; (6) outermost layer / base material layer / adhesive resin layer / innermost layer; (7) outermost layer / base material layer / adhesive resin layer / barrier layer / adhesive resin layer / thermoplastic resin layer / innermost layer; (8) outermost layer / base material layer / thermoplastic resin layer / adhesive resin layer / barrier layer / adhesive resin layer / innermost layer; (9) outermost layer / base material layer / thermoplastic resin layer / adhesive resin layer / barrier layer / adhesive resin layer / thermoplastic resin layer / innermost layer, etc., may be applicable. Further, at any given location in such lamination product, it is possible, optionally, to provide any functional layer, such as shading layer or printed pattern layer, etc., as mentioned later. Further, the lamination configuration

which has two or more of barrier layers which are layered via a intermediate layer, or layered directly may be adopted. Furthermore, with respect to the base material layer or other layers, embodiments which each has two or more of these layer may be adopted.

The outermost layer may be generally made of a thermoplastic resin, while the innermost layer may be generally made of a thermoplastic resin or an adhesive resin, as mentioned later.

When two or more layers in the lamination product have a similar properties, all of these layers may be made of one same material, or each layers may be made of separate materials.

Next, the construction of the carton for liquid according to the present invention will be described by using an example. As shown in Fig. 2, the lamination product A shown in Fig. 1 is subjected to creasing ruled lines 11 which are in accordance with the shape of the carton for liquid to be obtained and may be lengthwise, crosswise, and/or slantwise lines, while punching into a blank board B having tabs 12 for sticking or the like. Then, in order to prevent penetration and leaks of contents, end-face processing, such as, skive hemming processing, etc., is performed to the end face of the blank board B according to the conventional way, and which will be followed by superposing a face of edge portion 13 on the tabs 12 (See Fig. 2) of the opposite side of the blank board B, and frame processing or hot-air processing to the superposed layers in order to fuse the faces of resin

layers which construct the innermost layer 5 and the outermost layer 1 provided in the tab 12 and the opposite edge portion 13 respectively. Utilizing the fused faces, a body part sealing portion 14 is formed by frame seal or hot-air seal. Thus, a tubular sleeve C is manufactured.

Next, the tubular sleeve C thus manufactured is delivered to the food manufacturer, etc., where the contents to be packed is filled up, and the tubular sleeve C is supplied to a contents filling machine (not shown). On the filling machine, in advance of the content filling, the inner surface of the bottom of the sleeve C is heated by hot-air or the like in order to fuse the resin layer which constructs the innermost layer, and which is followed by press sealing in order to give a sealed bottom portion 15. Thus, a packaging container D having an opening portion 16 at the upper side thereof is obtained. After that, the packaging container D is filled with the contents 17 injected from the opening portion 16. Further, the inner surface of the top of the container D is heated by hot-air in order to fuse the resin layer which constructs the innermost layer, which is followed by press sealing in order to give a roof-shaped sealed top portion 18. Thus, the sealed carton E for liquid which is filled with contents 17 according to the present invention is obtained.

The above-mentioned instantiation is one embodiment of the carton for liquid according to the present invention, and the present invention is not limited thereto.

For example, in the present invention, it is possible

to adopt any shape, such as block shapes, tubular shape, and the like, as the shape of the carton for liquid, although such modifications are not illustrated as drawings herein.

Next, materials which construct the carton for liquid according to the present invention, method for manufacturing the carton will be described in detail.

As the outermost layer of the carton for liquid according to this invention, for example, various heat-sealable resins which can be fused by heat and can bond to each other, such as polyolefin type resins and the like are usable.

Concretely, for example, a low density polyethylene, a medium density polyethylene, a high density polyethylene, a straight chain (linear) low density polyethylene, an ethylene-a-olefin copolymer polymerized with a metallocene catalyst, a polypropylene, an ethylene-vinyl acetate copolymer, an ionomer resin, an ethylene-acrylic acid copolymer, an ethylene-ethyl acrylate copolymer, an ethylene-methacryl acid copolymer, an ethylene-methyl methacrylate copolymer, an ethylene-propylene copolymer, an methylpentene polymer, an polybutene polymer, an acid modified polyolefin resin which is prepared by modifying a polyolefin type resin such as polyethylene or polypropylene with an unsaturated carboxylic acid such as acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid or itaconic acid, a polyvinyl acetate type resin, a poly (meth)acrylic type resin, a polyvinyl chloride type resin,

or the like is usable.

Using one or more of above mentioned resins, the outermost layer can be prepared by melt extruding such resin or resins with extruders and laminating the extruded melted resin layer via anchor coat layer or the like. Alternatively, the outermost layer can be prepared by forming film or seat of the resin or resins, and dry laminating the film or seat on a face of paper base via adhesive agent layer for laminating, or laminating the film or seat on a face of paper base via extruded melted resin layer similarly extruded as above.

The outermost layer of this invention may have a thickness of about 5 to 200 μm, preferably, 10 to 100 μm.

As the paper base of the carton for liquid according to this invention, since it composes the fundamental raw material of the carton, the paper which has appropriate shape ability, flexibility, rigidity, pliant and hard to break, strength may be used. For example, a bleached or non-bleached paper base material having a high sizing property, or pure-white roll paper, kraft paper, paper board, converted paper or the like can be used. As the paper base, a paper base having a basis weight of about 80-600 g/m^2, preferably, of about 100-450 g/m^2 may be used. In this invention, the paper base can be optionally provided with any desired printing pattern such as alphabetic characters, graphic form, figure pattern, symbols and others, which can be formed by any conventional printing method.

It is possible to subject the face of the paper base

layer to any known surface treatment such as corona discharging treatment, flame treatment, anchor coat treatment or the like in order to improve the adhesion strength between the paper base and the barrier layer, outermost layer or other layer to be attached to the paper base.

In certain uses, as the paper base, other materials such as relatively thickened fibrous boards, resins, or other known materials may be used. When used such materials, the desired barrier property may be also expected by forming the same barrier layer.

Next, the barrier layer of the carton for liquid according to the present invention will be described. To form the barrier layer, at first, the resin composition is prepared by adding to one or more resin as a main ingredient of vehicle component one or more kind of inorganic lamellar compound, and optionally adding any additive, such as dispersant, filler, various stabilizers, curing agent, cross linking agent, lubricant, ultraviolet ray absorbent, coloring agent such as pigment or dye, etc., and also adding solvent and / or diluent, etc., and mixing the resultant thoroughly.

Then, by using the thus prepared resin composition, coating it on a face of the paper base with a coating method such as roll coating, gravure coating, knife coating, dip coating, spray coating, or the like, and then drying up the coated film in order to remove the solvent and / or diluent, etc., and optionally further subjecting the dried coating film to aging treatment, the barrier layer can be obtained

which consists of the coating film made of the resin composition which is comprised of the resin and the inorganic lamella compound.

The thickness of the barrier layer of this invention is desirable to be in the range of about 0.1 to 10.0g/m^2 (in dry condition), preferably, in the range of about 1.0 to 10.0g/m^2 (in dry condition).

Alternatively, the barrier layer can be formed by extrusion coating. In this case, at first, the resin composition is prepared by adding to one or more resin as a main ingredient of vehicle component one or more kind of inorganic lamellar compound, and optionally adding any additive, such as dispersant, filler, various stabilizers, curing agent, cross linking agent, lubricant, ultraviolet ray absorbent, coloring agent such as pigment or dye, etc., and also adding solvent and / or diluent, etc., and mixing the resultant thoroughly, as mentioned above.

Then, by using the thus prepared resin composition, fused extrusion coating it on a face of the paper base with an extruder such as T-die extruder or the like to form an extrusion coating film, the barrier layer can be obtained which consists of the coating film made of the resin composition which is comprised of the resin and the inorganic lamella compound.

The thickness of the barrier layer which consists of the above mentioned extrusion coating film is desirable to be in the range of about 1 to 100 μm, preferably, about 3.0

to 30.0 μm (in dry condition).

When the lamination product according to this invention is manufactured by laminating plural layers involving at least a barrier layer to the paper base, not only the above mentioned embodiment where the barrier layer is extrusion coated singly, but an another embodiment where the plural layers involving the barrier layer is simultaneously co-extrusion coated on the paper base with a co-extruder so as to form a multilayered co-extrusion coating is also adaptable. When such a multilayered co-extrusion coating is adapted, a common fused extrusion temperature can be used for all of the resins or resin compositions to be formed the respective layers. Alternatively, separate fused extrusion temperatures can be set for individual resins or resin compositions to be formed the layers. When such a multilayered co-extrusion coating is adapted in order to form plural layers involving the barrier layer onto the paper base, there is a possibility that the innermost layer made of polyolefin resin or the like for heat sealing will cause deterioration thereof by being exposed to a high temperature, although the deterioration is slightly, as mentioned later. Due to the deterioration, the heat sealablity may be degraded, and the odor transferring to the liquid contents after the package manufacturing may be caused. In order to prevent the deterioration of the innermost layer which is followed by such defects, it is possible to set the fused extrusion temperature low, or set the distance between the paper base and the die lip of the extruder short.

Alternatively, onto the exposed surface of the co-extruded multilayer product (e.g., the surface of a thermoplastic resin such as polyolefin resin for heat-sealing, to be form the innermost layer of the container), an additional layer made of a thermoplastic resin such as polyolefin resin for heat-sealing may be formed by the fused extrusion coating (See the aforementioned layer constructions of (5), (7) and (9)).

In stead of the above mentioned coating methods, the barrier layer can be formed by various stacking methods. In this case, at first, the resin composition is prepared by adding to one or more resin as a main ingredient of vehicle component one or more kind of inorganic lamellar compound, and optionally adding any additive, such as dispersant, filler, various stabilizers, curing agent, cross linking agent, lubricant, ultraviolet ray absorbent, coloring agent such as pigment or dye, etc., and also adding solvent and / or diluent, etc., and mixing the resultant thoroughly, as mentioned above.

Then, by using the thus prepared resin composition, forming it as a film or sheet with an extruder such as T-die extruder, inflation molding machine, casting machine, or the like, and then laminating the film or sheet thus obtained onto a face of the paper base via fused extruded resin layer in the extrusion stacking method, or via laminating adhesive agent layer in the dry laminating method, the barrier layer can be obtained which consists of the coating film made of

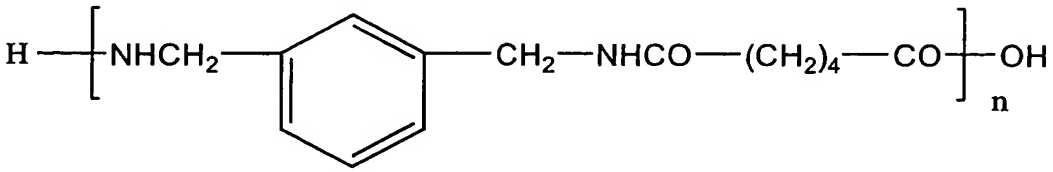
the resin composition which is comprised of the resin and the inorganic lamella compound.

The thickness of the barrier layer which consists of the above mentioned extrusion coating film is desirable to be in the range of about 1 to 100 μm, preferably, about 3.0 to 30.0 μm (in dry condition).

As the resin for the barrier layer, any resin which can function as a binder for the inorganic lamellar compound and the like can be used. For examples, polyethylene type resins, polypropylene type resins, polybutene-1, polystyrene type resins, acrylonitrile-styrene copolymers (AS resins), acrylonitrile-butadiene-styrene terpolymers (ABS resins), polyvinyl chloride type resins, polyvinyl acetate type resins, ethylene-vinyl acetate copolymers, poly(meth)acryl type resins, polycarbonate type resins, polyvinyl alcohol, ethylene-vinyl alcohol type resins, polyvinyl acetal, polyvinyl butyral, polyester type resins, unsaturated polyester resins, alkyd resins, polyamide type resins, epoxy type resins, phenol type resins, melamine type resins, urea resins, silicone type resins, polyurethane type resins, acetal type resins, cellulose type resins, or others, can be used singly or as any combination thereof.

Among the above listed resins, polyamide type resins, particularly, crystalline polyamides which possess the barrier property to oxygen gas and water vapor on its own and is superior in the extrusion moldability, more preferably the polymer represented by the following formula, typically,

Nylon MXD6 (Mitsubishi Gas Kagaku K.K.) are desirable in the present invention.



As the crystalline polyamide, for example, a crystalline polyamide type resin which is capable of being produced by a polycondensation reaction between an aromatic diamine such as metaxylenediamine or p-xylenediamine, and a dicarboxylic acid or derivative thereof such as adipic acid, suberic acid, sebacic acid, cyclohexane dicarboxylic acid, terephthalic acid or isophthalic acid, can be used.

Furthermore, in the present invention, it is desirable to use, as the resin for the barrier layer, a blend which is prepared by adding to the crystalline polyamide type resin one or more kind of aliphatic polyamide type resins for the sake of improving the extrusion property, or adhesiveness to the paper base and other films.

As the above mentioned aliphatic polyamide type resin, for example, aliphatic polyamide obtained by a polycondensation reaction between an aliphatic or alicyclic diamine such as hexamethylenediamine, decamethylene diamine, dodeca methylene diamine, 2, 2, 4- or 2, 4, 4-trimethyl hexamethylenediamine, 1, 3- or 1, 4-bis(aminomethyl) cyclohexane, or bis(p-aminocyclohexyl methane), and a dicarboxylic acid or derivative thereof such as adipic acid, suberic acid, sebacic acid, cyclohexane dicarboxylic acid,

terephthalic acid or isophthalic acid; polyamide resin obtained by condensation of ε-aminocaproic acid or 11-amino undecanoic acid; polyamide resin obtained from a lactam compound such as ε-caprolactam or ω-laurolactam; or a blend thereof can be used.

Concretely, the aliphatic polyamide type resin such as Nylon 6, Nylon 66, Nylon 9, Nylon 11, Nylon 12, Nylon 6 / 66, Nylon 66 / 610 can be used.

As the blending ratio of the crystalline aromatic polyamide type resin and aliphatic polyamide type resin, for example, a blending ratio of about 60 to 100 % by weight of crystalline aromatic polyamide type resin and about 0 to 40 % by weight of aliphatic polyamide type resin can be used, although it is not limited thereto.

Next, in the present invention, as an inorganic lamellar compound, any compound can be used, as long as the unit crystalline layers of the compound form the lamellar structure by mutually piling up, and the compound is capable of forming a secondary aggregate which has a larger size than the actual particle size of the inorganic lamellar compound by aggregating the lamellar structure, wherein the secondary aggregates can bring the gas barrier to the barrier layer when they are dispersed into the resin matrix. Concretely, one or more kind of crayey minerals can be used. As the crayey mineral, for example, kaolinite, dickite, nacrite, halloysite, antigorite, chrysotile, pyrophyllite, montmorillonite, beidellite, nontronite, saponite, sauconite, stevensite

hectorite, tetraslicic mica, sodium tenorite, muscovite, margarite, talc, vermiculite, phlogopite, xanthophylite, chlorite, and others, can be used singly or in any combination thereof.

The particle diameter of the inorganic lamellar compound is not paticularly limited, but it is desirable to have a size in the planar direction within the range of about 3 to 5000 nm, particularly, about 500 to 3000 nm in a state that the inorganic lamellar is subjected to completely delamination. In addition, it is desirable that the thickness of each layer of the inorganic lamellar compound is not more than 10nm, preferably, about 1 nm to 5nm, that the aspect ratio of the inorganic lamellar compound is in the range of 30 to 5000, preferably, 50 to 3000, since the good barrier property or other properties will be expected.

Further, it is desirable that the inorganic lamellar compound has the cation exchange capacity of not less than 30 meq / 100g, preferably, 50 to 200 meq / 100g, since it can be expected that the compound will be dispersed uniformly in the resin composition and a good gas barrier property will be obtained. However, the capacity is not limited thereto.

The inorganic lamellar compound may be optionally subjected to various surface treatments for improving the dispersion in the resin matrix. For example, it is preferable to give a chemical treatment with an organic ammonium salt such as aluminum stearate. Additionally, a method where a compound (including oligomer or polymer) which has both a

chain or fragment lyophilic to the resin matrix and a chain or fragment lyophilic to the inorganic lamellar compound is added to the resin composition, or a method where such amphipatic compound is coated or grafted to the inorganic lamellar compound are also adaptable.

In this invention, the blending ratio of the resin and the inorganic lamellar compound is not particularly limited since it can be varied by the kinds of the inorganic lamellar compound and the resin used. However, it is preferable that they are blended in the proportions of 1 part by weight inorganic lamellar compound to 2 - 100 parts by weight resin, preferably, 1 part by weight inorganic lamellar compound to 2 - 50 parts by weight resin, for instance.

Further, it is desirable that the volume ratio of (inorganic lamellar compound / resin) is in the range of (5/95) to (40/60), when forming the barrier layer. If such volume ratio is attained, good gas barrier property as well as a good film formability can be realized.

Next, the innermost layer of the carton for liquid according to the present invention will be described. As the innermost layer, for example, various heat-sealable resins which can be fused by heat and can bond to each other, such as polyolefin type resins and the like are usable, as is the case with the outermost layer.

Concretely, for example, a low density polyethylene, a medium density polyethylene, a high density polyethylene, a straight chain (linear) low density polyethylene, an

ethylene-a-olefin copolymer polymerized with a metallocene catalyst, a polypropylene, an ethylene-vinyl acetate copolymer, an ionomer resin, an ethylene-acrylic acid copolymer, an ethylene-ethyl acrylate copolymer, an ethylene-methacryl acid copolymer, an ethylene-methyl methacrylate copolymer, an ethylene-propylene copolymer, an methylpentene polymer, an polybutene polymer, an acid modified polyolefin resin which is prepared by modifying a polyolefin type resin such as polyethylene or polypropylene with an unsaturated carboxylic acid such as acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid or itaconic acid, a polyvinyl acetate type resin, a poly (meth)acrylic type resin, a polyvinyl chloride type resin, or the like is usable.

Using one or more of above mentioned resins, the innermost layer can be prepared by melt extruding such resins with extruders and laminating the extruded melted resin layers via anchor coat layer or the like, onto, for example, one face of the barrier layer. Alternatively, the innermost layer can be prepared by forming a film or seat of the resin or resins, and dry laminating the film or seat on a face of barrier layer via adhesive agent layer for laminating, or laminating the film or seat on a face of barrier layer via extruded melted resin layer similarly extruded as above.

The innermost layer of this invention may have a thickness of about 5 to 200 μm, preferably, 10 to 100 μm.

In the present invention, it is desirable to constitute

the innermost layer with ethylene-a-olefin copolymer polymerized with a metallocene catalyst.

As the ethylene-a-olefin copolymer polymerized with a metallocene catalyst, the ethylene-a-olefin copolymer which comes to copolymerize ethylene and an a-olefin with a catalyst utilizing a metallocene complex and alumoxane in combination, such as a combination of zirconocene dichloride and methylalumoxane, i. e., a metallocene catalyst, can be used, for example.

The above mentioned metallocene catalyst is also called the single site catalyst, since the active spot thereof is uniform, while the current used catalyst is called the multi-site catalyst, since the active spot thereof is uneven (Hereinafter, the metallocene catalyst is equivalent to a single site catalyst in their meanings.).

As the ethylene-a-olefin copolymer polymerized with a metallocene catalyst, concretely, the trade name " KERNEL " by Mitsubishi Chemical, Inc., the trade name "EVOLUE " by Mitsui Petrochemical Industries, Ltd., the trade name " EXACT" by EXXON CHEMICAL, USA, the trade name " AFFINITY " by DOW CHEMICAL, USA, and the trade name " ENGAGE", by DOW CHEMICAL, USA, can be used.

In this invention, the innermost layer made of ethylene-a-olefin copolymer polymerized with a metallocene catalyst can be formed by any one of known stacking methods which involves the fused extrusion laminating method where the innermost layer is laminated on a face of barrier layer

via an anchor coating layer, for example, and the dry laminating method where the innermost layer is laminated on a face of barrier layer via an laminating adhesive agent layer, for example.

The innermost layer of this invention may have a thickness of about 10 to 300 μm, preferably, 20 to 100 μm.

Now, the ethylene-a-olefin copolymer polymerized with a metallocene catalyst will be described more detailedly. As the ethylene-a-olefin copolymer polymerized with a metallocene catalyst, the ethylene-a-olefin copolymer which comes to copolymerize ethylene and a-olefin with a catalyst utilizing a metallocene type transition-metals compound and an organic aluminum compound in combination, i.e., a metallocene catalyst (involving the so-called Kaminsky catalyst) can be used. The above-mentioned metallocene catalyst may be supported and used with an inorganic substance. As the metallocene type transition-metal compound in the above embodiment , for example, those in which one or two groups selected by the family consisting of cyclopentadienyl group, substituted cyclopentadienyl group, indenyl group, substituted indenyl group, tetrahydro indenyl group, substituted tetrahydro indenyl group, furonyl group, and substituted furonyl group are bound to, or a cross linkage which is formed with two groups selected from the family being covalent bound each other is bound to, a transition metal which are selected from the IVB group, such as, titanium (Ti), a zirconium (Zr), and a hafnium (Hf); and which also has

substituent(s) involving hydrogen atom, oxygen atom, halogen atoms, alkyl groups, alkoxy groups, aryl groups, acetylacetonato groups, carbonyl groups, nitrogen molecule, oxygen molecule, Lewis bases, silicon atom, and / or ligand(s) such as unsaturated hydrocarbons, can be used.

Moreover, as the organic aluminum compound, alkylaluminum or chain or cyclic aluminoxane, etc., can be used. As the alkylaluminum, triethylaluminum, triisobutylaluminum, dimethyl aluminum chloride, a diethylaluminium chloride, methyl aluminum dichloride, ethyl aluminum dichloride, dimethyl aluminum fluoride, diisobutyl aluminum hydride, a diethyl aluminum hydride, ethylaluminum sesquichloride, etc. can be used, for example.

As the chain or cyclic aluminoxane, those which is obtained by contacting alkylaluminum with water can be used, for example.

For example, it may be produced by adding alkylaluminum at the time of a polymerization, and thereafter adding water, or by reacting the crystalline water of complex salt, or the water adsorbed in the organic or inorganic compound with alkylaluminum.

As the inorganic substance to which the metallocene catalyst is supported, silica gel, zeolite, silicon soil, etc. can be used, for example.

As the polymerization method for the copolymer, various kinds of polymerization methods, such as a bulk polymerization, solution polymerization, suspension polymerization, and a

vapor phase polymerization, can be used, for example.

The polymerization can be carried out in any method such as a batch method or continuous method. As the polymerization conditions, a polymerization temperature of -100°C to 250°C, a polymerization time of 5 minutes to 10 hours, and a reaction pressure of ordinary pressure to 300 kg/cm^2 are adaptable. Further, as the a-olefin comonomer to be copolymerized with ethylene, propylene, 1-butene, 3-methyl-1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, decene, etc., can be used, for example.

The above mentioned a-olefins may be used singly or in any combination thereof.

The mixing ratio of the a-olefin to the ethylene is desirable to be 1 to 50 % by the weight, preferably 10 to 30 % by the weight, for example.

The physical properties of the ethylene-a-olefin copolymer which carried out the polymerization using the above mentioned metallocene catalyst in the present invention are the molecular weight of 5×10^3 to 5×10^6, the density of 0.890 to 0.930 g/cm^3, and the melt flow rate [MFR] of about 0.1 to 50g / 10 minutes.

In the present invention, an anti-oxidant, an ultraviolet ray absorbent, an antistatic agent, an anti blocking agent, lubricant (fatty acid amide etc.), a flameproofing agent, inorganic or organic filler, a dye, a pigment, etc. can be added optionally to the ethylene-a-olefin copolymer obtained by the polymerization using the

metallocene catalyst.

In the present invention, as the innermost layer made of the ethylene-a-olefin copolymer obtained by the polymerization using the metallocene catalyst, a co-extruded resins layered film which consists of a ethylene-a-olefin copolymer polymerized with such a metallocene catalysts, and a polyolefin type resin, such as low density polyethylene or straight chain low density polyethylene, and which designates the layer of the ethylene-a-olefin copolymer polymerized with such a metallocene catalysts as an innermost layer can be used.

As the method for manufacturing the co-extruded resins layered film, the T-die co-extrusion method, or co-extrusion inflation method, or the like may be adaptable. The layer structure of the film consists of two or more layers which are co-extruded. And, it is desirable that the thickness of each resin layers are adjusted to arbitrarily within the range of about 2 to 20 μm.

As described above, the innermost layer is typically prepared by using heat-sealable resin which can be fused by heat and can bond to each other, concretely, for example, polyolefin type resin such as low density polyethylene, straight chain (linear) low density polyethylene, etc. Since the seal temperature using for the polyolefin type resin such as low density polyethylene, straight chain (linear) low density polyethylene is about 320 to 350 °C that is an extremely high temperature as the seal temperature, the pin-hole defect

will come about, and which defect induces poor sealing, fluid leak, etc.

Therefore, in the present invention, we focus attention on the ethylene-a-olefin copolymer which is polymerized using the metallocene catalyst and which has a low-temperature seal property. When the innermost layer is formed by the copolymer, it is possible to seal at a low temperature of about 250°C to about 300°C, and thus to prevent generating of a pinhole, and to avoid a poor seal, a liquid leak, etc.

Furthermore, the ethylene-a-olefin copolymer polymerized using the metallocene catalyst has the advantage that it has a paucity of propagation of fracture since it has adhesiveness, which results in the improvement of impact resistance. In addition, since the innermost layer is always contact with the contents, it is effective also to prevent degradation of anti-environmental stress-cracking property.

Moreover, in this invention, it is possible to blend the ethylene-a-olefin copolymer polymerized using the metallocene catalyst with any other polymer. For example, to blend it with an ethylene-butene copolymer, or so, will contribute to improve the tearing property and the easy opening, although there is an inclination that a slight degradation will be observed on the thermal resistance and that a reduction will be observed on the seal stability at a high temperature.

In the present invention, when an ethylene-a-olefin copolymer polymerized using the metallocene catalyst is used as the innermost layer, it will obtain a great advantage that

the heat-sealing can be completed even at a low temperature on the manufacturing of the carton for liquid.

As the material which forms the lamination product which constitutes the carton for liquid according to the present invention, for example, a resin film or sheet which has barrier properties to steam and water, etc, such as a low density polyethylene, medium density polyethylene, high density polyethylene, straight chain low density polyethylene, polypropylene, and ethylene-propylene copolymer; a resin film or sheet which has barrier properties to oxygen and steam, etc, such as polyvinylidene chloride type resin, polyvinyl alcohol type resin, ethylene-vinylalcohol copolymer, MXD polyamide type resin and polynaphthalene terephthalate type resin; and a colored resin film or sheet which has a shading property and which is made by adding to resin a coloring agent such as pigment and optionally any desirable additive and kneading the mixture are usable.

These materials may be used singly or in combination. The thickness of abovementioned film or sheet is not particularly limited, but it is usually desirable to be 5μm to 300 μm, and more preferably, 10 μm to 100 μm.

Since the packaging container is usually subjected to a severe condition with respect to both of physical and chemical standpoints, a severe suitability for packaging will be required to the lamination product in the present invention. In addition, various conditions, such as anti-deformation strength, drop and impact resistant strength, anti-pinhole

property, thermal resistance, sealing property, contents' quality integrity, workability, hygiene property, etc., are required. Therefore, in this invention, it is possible to choose and use any material capable of satisfying the above mentioned conditions. Concretely, a selection can be performed optimally among any known resinous sheet or film, involving low density polyethylene, medium density polyethylene, high density polyethylene, linear low density polyethylene, polypropylene, ethylene-propylene copolymer, ethylene-vinylacetate copolymer, ionomer resin, ethylene-ethyl acrylate copolymer, ethylene-(meth)acrylic acid copolymer, methylpentene polymer, polybutene type resin, polyvinyl chloride type resin, polyvinyl acetate type resin, polyvinylidene chloride type resin, a vinyl chloride-vinylidene chloride copolymer, poly(meth)acrylic resin, poly acrylic nitril type resin, polystyrene type resin, acrylonitrile-styrene copolymer (AS type resin), acrylonitrile-butadiene-styrene copolymer (ABS type resin), polyester type resin, polyamide type resin, polycarbonate type resin, polyvinyl alcohol type resin, saponified ethylene-vinylacetate copolymer, fluorine type resin, diene type resin, polyacetal type resin, polyurethane type resin, nitrocellulose, and others. In the present invention, the above mentioned film or sheet may be an unorientated one, monoaxially oriented one, biaxially oriented one, or others.

Moreover, the thickness thereof can be determined arbitrarily, but, preferably determined from the range of

several μm to about 300 μm.

Furthermore, in the present invention, the film or sheet interested may be of any material property, involving extrusion membrane formation, inflation membrane formation, and coating membrane formation. Alternatively, films, such as cellophane, a synthetic paper, etc. can be used.

Next, in the present invention, a desired printed pattern layer can be formed between any two layers in the he lamination product which constitutes the carton for liquid according to the present invention. The printed pattern layer, may be formed, for example, on the above mentioned coated film or sheet having barrier properties, with a desired printed pattern , such as alphabetic character, graphic form, design pattern, symbol, or others, by using an ordinary rotogravure ink composition, an ordinary offset ink composition, an ordinary letterpress ink composition, an ordinary screen ink composition or any other ink composition and performing a gravure method, an offset-printing method, a letterpress printing method, a silk screen printing method, or any other printing method, correspondingly.

Referring to the above mentioned ink composition, as a vehicle to be included in the ink composition, for example, polyolefin type resin, such as polyethylene type resin and chlorinated polypropylene resin; poly(meth)acrylic resin; polyvinyl chloride type resin; polyvinyl acetate type resin; vinyl chloride-vinyl acetate copolymer; polystyrene type resin; styrene-butadiene copolymer; vinylidene fluoride type

resin; polyvinyl alcohol type resin; polyvinyl acetal type resin; polyvinyl butyral type resin; poly butadiene type resin; polyester type resin, polyamide type resin; alkyd resin; epoxy type resin; unsaturated polyester type resin; thermosetting poly(meth)acrylic resin; melamine type resin; urea type resin; polyurethane type resin; phenol type resin; xylene type resin; maleic resin; cellulose type plastic, such as nitro cellulose, ethyl cellulose, acetyl butyl cellulose, and ethyloxyethyl cellulose; rubber type resin such as chlorinated rubber, and cyclized rubber; petroleum type resin; natural resin such as rosin, and casein; and fats and oils such as linseed oil, and soybean oil; and others can be used singly or in combination..

In the present invention, a ink composition may be used which comprises one or more of the aforementioned vehicles as a principal ingredient, and one or more of coloring agents involving various dyes and pigments, and optionally, any additives such as a bulking agent, a stabilizing agent, a plasticizer, an antioxidant, an light stabilizer such as an ultraviolet ray absorbent, a dispersant, a thickener, a drying agent, a lubricant, an antistatic agent, a cross linking agent, and other additives, wherein the ingredients are sufficiently kneaded with a solvent, a diluent, etc.

Next, the method for manufacturing the lamination product using the above ingredients will be explained. As such method, any ordinary laminating method for lamination product can be used, such as, a wet lamination process, a

dry lamination process, a non-solvent type dry lamination process, an extrusion lamination process, a T-die extrusion method, the aforementioned co-extrusion lamination process, an inflation process, a co-extrusion inflation process.

In the present invention, if desired, it is possible to adapt any preliminary treatment, such as corona treatment, plasma treatment, ozonization, etc., in advance of the aforementioned lamination process. Moreover, if desired, it is also possible to use any anchor coat agent, such as isocyanate type (urethane type), polyethyleneimine type, polybutadiene type, and an organic titanium type; or any ordinary adhesive agent for lamination, such as polyurethane type, polyacryl type, polyester type, epoxy type, polyvinyl acetate type, cellulose type, etc.

As the method for manufacturing the lamination product according to the present invention, a dry lamination process which carries out a laminating through an adhesives layer of the adhesive agent for a lamination, or an extrusion lamination process which carries out a laminating through a fused extrusion resin layer using the adhesive resin for melting extrusion, or the aforementioned co-extrusion lamination process, etc., may be adaptable concretely.

In the above, as the adhesive agent for lamination, any one-pack or two-pack; hardening or non-hardening; solvent type, aqueous type, or emulsion type adhesive agent, such as vinyl type, (meth)acrylic type, polyamide type, polyester type, polyether type, polyurethane type, epoxy type, rubber

type, etc., may be adaptable.

As a method for coating the adhesive agent for lamination, the direct gravure roll coat method, the gravure roll coat method, the kisscoat method, the reverse roll coat method, the phonten method, the transfer roll coat method, and the other approaches may be adaptable, for example.

The coating amount may be 0.1 - 10 g/m^2 (in dry state), more preferably, 1 - 5 g/m^2 (in dry state). In addition, to the above mentioned adhesive agent for lamination, an adhesion promoter, such as a silane coupling agent, can be added optionally.

As the adhesive resin for melting extrusion, the above mentioned polyolefin type resin having the heat-sealability may be similarly adaptable, and among them, low density polyethylene, particularly, linear low density polyethylene and acid modified polyethylene, are preferable.

The thickness of the fused extrusion resin layer using the adhesive resin for melting extrusion may be about 5 to 100 μm, particularly, 10 to 50 μm.

In the present invention, when rugged bonding strength is required on the abovementioned lamination, to coat an adhesion amelioration agent, such as an anchor coat agent, etc. can also be carried out.

As the above mentioned anchor coat agent, various kinds of anchor coat agents involving organic titanium type anchor coat agents such as alkyl titanate, isocyanate type anchor coat agents, polyethyleneimine type anchor coat agents,

polybutadiene type anchor coat agents, and any other aqueous or oleaginous anchor coat agents may be adaptable.

In the present invention, the above mentioned anchor coat agent can be coated by any coating method, such as roll coating, gravure coating, knife coating, dip coating, spray coating, etc., and then the solvent, the diluent, and the like are evaporated from the coating in order to obtain the anchor coat agent layer.

As coverage of the above mentioned anchor coat agent, about 0.1 to 5 g/m^2 (in dry state) is desirable.

As the carton for liquid according to the present invention, for example, a brick type, a flat type, or a gable top type, etc. can be manufactured. Moreover, the shape of the carton is not limited and is arbitrary, and thus any shape involving square containers, round shaped containers, cylindrical shaped paper cans, etc., can be manufactured.

To the carton for liquid according to the present invention, various foods and drinks, various chemicals such as adhesive agent and sticker, various general goods involving cosmetics and drugs, and etc., may be charged and packaged.

Particularly, the carton for liquid according to the present invention is of great value as packaging container for charging and packing any liquid drink or food, such as liquor, juice or soft drink, mineral water, liquid seasoning such as soy-sauce, sauce, or soup, and the like.

EXAMPLES

Now, the present invention will be described more concretely with reference to the following examples. It should be understood that the following example are disclosed only for the purpose of facilitating the comprehension and explanation for the present invention, and thus the spirit and scope of the present invention are never limited to the disclosed Examples.

Example 1

(1) A paper base having a basis weight of 340 g/m^2 was used as a support, and a low density polyethylene resin (density: 0.923g/cc, melt index (MI)=3.7, m.p.=111°C) was fused and extrusion laminated on one surface side of the paper using an extruder in order to form 20 μm thick low density polyethylene resin layer.

Another surface side of the paper base is subjected to a corona discharge treatment. Thereafter, on the thus corona discharge treated surface, a resinous composition which was prepared by adequately mixing 98 parts by weight of fused crystalline polyamide (Nylon MXD6 grade 6007, mfd. by Mitsubishi Gas Kagaku K.K.) with 2 parts by weight of inorganic lamellar compound (Kunipia F, mfd. by Kunimine Industries, Inc., a montmorillonite type clay mineral), was fused and extruded by an extruder, in order to form a 30 μm thick barrier layer.

Next, onto the exposed surface of the thus formed barrier layer, an anchor coat agent (A3210/A3075, mfd. by

Takeda Chemical Industries, Ltd) was coated using the gravure coat method, and then it was dried with a dryer at 80°C in order to obtain an anchor coat layer having a coated amount of 1 g/m^2 (in dry state). Further, onto a surface of the anchor coat layer, a low density polyethylene resin (density: 0.923g/cc, melt index (MI) =3.7, m.p. =111°C) was fused and extrusion laminated using an extruder in order to form 30 μm thick low density polyethylene resin layer.

(2) Then, the lamination product manufactured as above was subjected to creasing ruled lines which were in accordance with the shape of a gable top type carton for liquid to be obtained and may be lengthwise, crosswise, and/or slantwise lines, while punching into a blank board having tabs for sticking. Then, in order to prevent penetration and leaks of contents, the skive hemming processing as an end-face processing was performed to the end faces of the blank board. After that, the hot-air processing was performed to the tabs for sticking in order to fuse the low density polyethylene film of the tab for sticking, and which was followed by superposing another edge portion of the blank board onto the fused face in order to paste them together and to form a body part sealing portion. Thus, a tubular sleeve was manufactured.

Next, the inner surface of the bottom of the tubular sleeve thus manufactured was heated by hot-air in order to fuse the low density polyethylene film of the inner surface, and which was followed by press sealing in order to give a sealed bottom portion. After that, from the opening portion

of the opposite side, fruit juice is injected. After the injection, the inner surface of the top of the container was heated by hot-air in order to fuse the low density polyethylene film of the inner surface, which was followed by press sealing in order to give a sealed gable top portion. Thus, the sealed carton for liquid which was filled with contents according to the present invention was obtained.

It was found that the sealed liquid carton manufactured as above did not suffer the occurrence of pin-hole caused by heat. It was also excellent in the barrier property capable of inhibiting penetration of oxygen gas, steam, etc., and excellent in the flavor retention, and it was able to prevent deterioration of contents, and it was also excellent in the laminate strength, it was adequate for bearing transportation in the market, and it was excellent in the preservative property or keeping quality.

Example 2

(1) A paper base having a basis weight of 340 g/m^2 was used as a support, and a low density polyethylene resin (density: 0.923g/cc, melt index (MI)=3.7, m.p.=111°C) was fused and extrusion laminated on one surface side of the paper using an extruder in order to form 20 μm thick low density polyethylene resin layer.

Another surface side of the paper base is subjected to a corona discharge treatment. Thereafter, on the thus corona discharge treated surface, a resinous composition

which was prepared by adequately mixing fused resin comprising 50 parts by weight of fused crystalline polyamide (Nylon MXD6 grade 6007, mfd. by Mitsubishi Gas Kagaku K.K.) and 48 parts by weight of aliphatic nylon (SF1018A, mfd. by Ube Industries, Ltd.) with 2 parts by weight of inorganic lamellar compound (Kunipia F, mfd. by Kunimine Industries, Inc., a montmorillonite type clay mineral), was fused and extruded by an extruder, in order to form a 30 μm thick barrier layer.

Next, onto the exposed surface of the thus formed barrier layer, an anchor coat agent (A3210/A3075, mfd. by Takeda Chemical Industries, Ltd) was coated using the gravure coat method, and then it was dried with a dryer at 80°C in order to obtain an anchor coat layer having a coated amount of 1 g/m^2 (in dry state). Further, onto a surface of the anchor coat layer, a low density polyethylene resin (density: 0.923g/cc, melt index (MI) =3.7, m.p. =111°C) was fused and extrusion laminated using an extruder in order to form 30 μm thick low density polyethylene resin layer.

(2) Then, the lamination product manufactured as above was subjected to creasing ruled lines which were in accordance with the shape of a gable top type carton for liquid to be obtained and may be lengthwise, crosswise, and/or slantwise lines, while punching into a blank board having tabs for sticking. Then, in order to prevent penetration and leaks of contents, the skive hemming processing as an end-face processing was performed to the end faces of the blank board. After that, the hot-air processing was performed to the tabs

for sticking in order to fuse the low density polyethylene film of the tab for sticking, and which was followed by superposing another edge portion of the blank board onto the fused face in order to paste them together and to form a body part sealing portion. Thus, a tubular sleeve was manufactured.

Next, the inner surface of the bottom of the tubular sleeve thus manufactured was heated by hot-air in order to fuse the low density polyethylene film of the inner surface, and which was followed by press sealing in order to give a sealed bottom portion. After that, from the opening portion of the opposite side, fruit juice is injected. After the injection, the inner surface of the top of the container was heated by hot-air in order to fuse the low density polyethylene film of the inner surface, which was followed by press sealing in order to give a sealed gable top portion. Thus, the sealed carton for liquid which was filled with contents according to the present invention was obtained.

It was found that the sealed liquid carton manufactured as above did not suffer the occurrence of pin-hole caused by heat. It was also excellent in the barrier property capable of inhibiting penetration of oxygen gas, steam, etc., and excellent in the flavor retention, and it was able to prevent deterioration of contents, and it was also excellent in the laminate strength, it was adequate for bearing transportation in the market, and it was excellent in the preservative property or keeping quality.

Example 3

(1) A paper base having a basis weight of 340 g/m^2 was used as a support, and a low density polyethylene resin (density: 0.923g/cc, melt index (MI)=3.7, m.p.=111°C) was fused and extrusion laminated on one surface side of the paper using an extruder in order to form 20 μm thick low density polyethylene resin layer.

Another surface side of the paper base is subjected to a corona discharge treatment. Thereafter, directly on the thus corona discharge treated surface, a thermoplastic resin layer (15 μm thick) made of low density polyethylene (Mirason 11P, melt index (MI)=7.2, mfd. by Mitsui Chemical Co. Ltd.), an adhesive layer (10 μm thick) made of adhesive polyolefin (ADMER NF548, mfd. by Mitsui Chemical Co. Ltd.), a barrier resin layer (10 μm thick)made of a barrier rein mentioned later, another adhesive layer (10 μm thick) made of adhesive polyolefin (ADMER NF548, mfd. by Mitsui Chemical Co. Ltd.), and another thermoplastic resin layer (innermost layer) (15 μm thick) made of low density polyethylene (Mirason 11P, melt index (MI)=7.2, mfd. by Mitsui Chemical Co. Ltd.) were coextruded (extrusion temperature: 300°C) from dies of a monoaxial coextruder (CO-EC machine) so as to provide a five-layer structure and to be laminated in this order, thereby the lamination product was prepared.

As the barrier resin, a composition was used which was prepared by blending 90 parts by weight of fused crystalline polyamide (Nylon MXD6 grade 6011, mfd. by Mitsubishi Gas Kagaku

K.K.) with 10 parts by weight of montmorillonite (Kunipia F, mfd. by Kunimine Industries, Inc., size of the planar direction: 100 - 1000 nm, layer thickness: 1 nm, aspect ratio: 100 - 1000, cation exchange capacity: 115 meq/100g) as the inorganic lamellar compound which was treated in advance with a stearyl ammonium salt having a carboxyl acid reactive terminal group in 2.5 times equivalent amount as much as the cation exchange capacity of the inorganic lamellar compound, and mixing them in molten state.

(2) Then, the lamination product manufactured as above was subjected to creasing ruled lines which were in accordance with the shape of a gable top type carton for liquid to be obtained and may be lengthwise, crosswise, and/or slantwise lines, while punching into a blank board having tabs for sticking. Then, in order to prevent penetration and leaks of contents, the skive hemming processing as an end-face processing was performed to the end faces of the blank board. After that, the hot-air processing was performed to the tabs for sticking in order to fuse the low density polyethylene film of the tab for sticking, and which was followed by superposing another edge portion of the blank board onto the fused face in order to paste them together and to form a body part sealing portion. Thus, a tubular sleeve was manufactured.

Next, the inner surface of the bottom of the tubular sleeve thus manufactured was heated by hot-air in order to fuse the low density polyethylene film of the inner surface, and which was followed by press sealing in order to give a

sealed bottom portion.

It was found that the sealed liquid carton manufactured as above did not suffer the occurrence of pin-hole caused by heat. It was also excellent in the barrier property capable of inhibiting penetration of oxygen gas, steam, etc., and excellent in the flavor retention, and it was able to prevent deterioration of contents, and it was also excellent in the laminate strength, it was adequate for bearing transportation in the market, and it was excellent in the preservative property or keeping quality.

Example 4

(1) A paper base having a basis weight of 340 g/m^2 was used as a support, and a low density polyethylene resin (density: 0.923g/cc, melt index (MI)=3.7, m.p.=111°C) was fused and extrusion laminated on one surface side of the paper using an extruder in order to form 20 μm thick low density polyethylene resin layer.

Another surface side of the paper base is subjected to a corona discharge treatment. Thereafter, directly on the thus corona discharge treated surface, a barrier resin layer (10 μm thick) made of a barrier rein mentioned later, an adhesive layer (10 μm thick) made of adhesive polyolefin (ADMER NF548, mfd. by Mitsui Chemical Co. Ltd.), and an thermoplastic resin layer (innermost layer) (15 μm thick) made of low density polyethylene (Mirason 11P, melt index (MI)=7.2, mfd. by Mitsui Chemical Co. Ltd.) were coextruded (extrusion temperature:

300°C) from dies of a monoaxial coextruder (CO-EC machine) so as to provide a three-layer structure and to be laminated in this order, thereby the lamination product was prepared.

As the barrier resin, a composition was used which was prepared by blending 90 parts by weight of fused crystalline polyamide (Nylon MXD6 grade 6011, mfd. by Mitsubishi Gas Kagaku K.K.) with 10 parts by weight of montmorillonite (Kunipia F, mfd. by Kunimine Industries, Inc., size of the planar direction: 100 - 1000 nm, layer thickness: 1 nm, aspect ratio: 100 - 1000, cation exchange capacity: 115 meq/100g) as the inorganic lamellar compound which was treated in advance with a stearyl ammonium salt having a carboxyl acid reactive terminal group in 2.5 times equivalent amount as much as the cation exchange capacity of the inorganic lamellar compound, and mixing them in molten state.

(2) Then, the lamination product manufactured as above was subjected to creasing ruled lines which were in accordance with the shape of a gable top type carton for liquid to be obtained and may be lengthwise, crosswise, and/or slantwise lines, while punching into a blank board having tabs for sticking. Then, in order to prevent penetration and leaks of contents, the skive hemming processing as an end-face processing was performed to the end faces of the blank board. After that, the hot-air processing was performed to the tabs for sticking in order to fuse the low density polyethylene film of the tab for sticking, and which was followed by superposing another edge portion of the blank board onto the

fused face in order to paste them together and to form a body part sealing portion. Thus, a tubular sleeve was manufactured.

It was found that the sealed liquid carton manufactured as above did not suffer the occurrence of pin-hole caused by heat. It was also excellent in the barrier property capable of inhibiting penetration of oxygen gas, steam, etc., and excellent in the flavor retention, and it was able to prevent deterioration of contents, and it was also excellent in the laminate strength, it was adequate for bearing transportation in the market, and it was excellent in the preservative property or keeping quality.

Control 1

(1) A paper base having a basis weight of 340 g/m^2 was used as a support, and a low density polyethylene resin (density: 0.923g/cc, melt index (MI)=3.7, m.p.=111°C) was fused and extrusion laminated on one surface side of the paper using an extruder in order to form 20 μm thick low density polyethylene resin layer.

Another surface side of the paper base is subjected to a corona discharge treatment. Thereafter, on the thus corona discharge treated surface, a resinous composition comprising 100 parts by weight of crystalline polyamide (Nylon MXD6 grade 6007, mfd. by Mitsubishi Gas Kagaku K.K.) was fused and extruded by an extruder, in order to form a 30 μm thick barrier layer.

Next, onto the exposed surface of the thus formed

barrier layer, an anchor coat agent (A3210/A3075, mfd. by Takeda Chemical Industries, Ltd) was coated using the gravure coat method, and then it was dried with a dryer at 80°C in order to obtain an anchor coat layer having a coated amount of 1 g/m^2 (in dry state). Further, onto a surface of the anchor coat layer, a low density polyethylene resin (density: 0.923g/cc, melt index (MI) =3.7, m.p. =111°C) was fused and extrusion laminated using an extruder in order to form 30 μm thick low density polyethylene resin layer.

(2) Then, the lamination product manufactured as above was subjected to creasing ruled lines which were in accordance with the shape of a gable top type carton for liquid to be obtained and may be lengthwise, crosswise, and/or slantwise lines, while punching into a blank board having tabs for sticking. Then, in order to prevent penetration and leaks of contents, the skive hemming processing as an end-face processing was performed to the end faces of the blank board. After that, the hot-air processing was performed to the tabs for sticking in order to fuse the low density polyethylene film of the tab for sticking, and which was followed by superposing another edge portion of the blank board onto the fused face in order to paste them together and to form a body part sealing portion. Thus, a tubular sleeve was manufactured.

Next, the inner surface of the bottom of the tubular sleeve thus manufactured was heated by hot-air in order to fuse the low density polyethylene film of the inner surface, and which was followed by press sealing in order to give a

sealed bottom portion. After that, from the opening portion of the opposite side, fruit juice is injected. After the injection, the inner surface of the top of the container was heated by hot-air in order to fuse the low density polyethylene film of the inner surface, which was followed by press sealing in order to give a sealed gable top portion. Thus, the sealed carton for liquid which was filled with contents was obtained.

Control 2

(1) A paper base having a basis weight of 340 g/m^2 was used as a support, and a low density polyethylene resin (density: 0.923g/cc, melt index (MI)=3.7, m.p.=111°C) was fused and extrusion laminated on one surface side of the paper using an extruder in order to form 20 μm thick low density polyethylene resin layer.

Another surface side of the paper base is subjected to a corona discharge treatment. Thereafter, on the thus corona discharge treated surface, a resinous composition which was prepared by adequately kneading 50 parts by weight of crystalline polyamide (Nylon MXD6 grade 6007, mfd. by Mitsubishi Gas Kagaku K.K.) and 50 parts by weight of aliphatic nylon (SF1018A, mfd. by Ube Industries, Ltd.) was fused and extruded by an extruder, in order to form a 30 μm thick barrier layer.

Next, onto the exposed surface of the thus formed barrier layer, an anchor coat agent (A3210/A3075, mfd. by Takeda Chemical Industries, Ltd) was coated using the gravure

coat method, and then it was dried with a dryer at 80°C in order to obtain an anchor coat layer having a coated amount of 1 g/m^2 (in dry state). Further, onto a surface of the anchor coat layer, a low density polyethylene resin (density: 0.923g/cc, melt index (MI) =3.7, m.p. =111°C) was fused and extrusion laminated using an extruder in order to form 30 μm thick low density polyethylene resin layer.

(2) Then, the lamination product manufactured as above was subjected to creasing ruled lines which were in accordance with the shape of a gable top type carton for liquid to be obtained and may be lengthwise, crosswise, and/or slantwise lines, while punching into a blank board having tabs for sticking. Then, in order to prevent penetration and leaks of contents, the skive hemming processing as an end-face processing was performed to the end faces of the blank board. After that, the hot-air processing was performed to the tabs for sticking in order to fuse the low density polyethylene film of the tab for sticking, and which was followed by superposing another edge portion of the blank board onto the fused face in order to paste them together and to form a body part sealing portion. Thus, a tubular sleeve was manufactured.

Next, the inner surface of the bottom of the tubular sleeve thus manufactured was heated by hot-air in order to fuse the low density polyethylene film of the inner surface, and which was followed by press sealing in order to give a sealed bottom portion. After that, from the opening portion of the opposite side, fruit juice is injected. After the

injection, the inner surface of the top of the container was heated by hot-air in order to fuse the low density polyethylene film of the inner surface, which was followed by press sealing in order to give a sealed gable top portion. Thus, the sealed carton for liquid which was filled with contents according to the present invention was obtained.

Control 3

(1) A paper base having a basis weight of 340 g/m^2 was used as a support, and a low density polyethylene resin (density: 0.923g/cc, melt index (MI)=3.7, m.p.=111°C) was fused and extrusion laminated on one surface side of the paper using an extruder in order to form 20 μm thick low density polyethylene resin layer.

Another surface side of the paper base is subjected to a corona discharge treatment. Thereafter, on the thus corona discharge treated surface, a resinous composition comprising 100 parts by weight of aliphatic nylon (SF1018A, mfd. by Ube Industries, Ltd.) was fused and extruded by an extruder, in order to form a 30 μm thick barrier layer.

Next, onto the exposed surface of the thus formed barrier layer, an anchor coat agent (A3210/A3075, mfd. by Takeda Chemical Industries, Ltd) was coated using the gravure coat method, and then it was dried with a dryer at 80°C in order to obtain an anchor coat layer having a coated amount of 1 g/m^2 (in dry state). Further, onto a surface of the anchor coat layer, a low density polyethylene resin (density:

0.923g/cc, melt index (MI) =3.7, m.p. =111°C) was fused and extrusion laminated using an extruder in order to form 30 μm thick low density polyethylene resin layer.

(2) Then, the lamination product manufactured as above was subjected to creasing ruled lines which were in accordance with the shape of a gable top type carton for liquid to be obtained and may be lengthwise, crosswise, and/or slantwise lines, while punching into a blank board having tabs for sticking. Then, in order to prevent penetration and leaks of contents, the skive hemming processing as an end-face processing was performed to the end faces of the blank board. After that, the hot-air processing was performed to the tabs for sticking in order to fuse the low density polyethylene film of the tab for sticking, and which was followed by superposing another edge portion of the blank board onto the fused face in order to paste them together and to form a body part sealing portion. Thus, a tubular sleeve was manufactured.

Next, the inner surface of the bottom of the tubular sleeve thus manufactured was heated by hot-air in order to fuse the low density polyethylene film of the inner surface, and which was followed by press sealing in order to give a sealed bottom portion. After that, from the opening portion of the opposite side, fruit juice is injected. After the injection, the inner surface of the top of the container was heated by hot-air in order to fuse the low density polyethylene film of the inner surface, which was followed by press sealing in order to give a sealed gable top portion. Thus, the sealed

liquid carton which was filled with contents was obtained.

Measurement of oxygen permeability

With respect to the individual liquid cartons manufactured by aforementioned Examples 1 - 4 and Controls 1 - 3, the oxygen permeability was determined.

(1) Measurement of oxygen permeability

This property was measured about (a) lamination products and (b) liquid cartons, under a temperature of 23°C and a humidity of 40% RH by use of a measuring device (OXTRAN, mfd. by MOCON, USA). The results obtained are shown in Table 1.

Table 1

	Oxygen permeability	
	Lamination product	Liquid Carton
Example 1	5.0	1.5
Example 2	7.3	2.0
Control 1	10.5	4.0
Control 2	22.0	10.0
Control 3	65.0	25.0

In Table 1, the units of the oxygen permeability for the lamination product and the liquid carton are [cc/m^2/day (at 23 °C and 90% RH)] and [cc/pkg/day at 23 °C and 90% RH], respectively.

As clear from the measurement results shown in Table 1, the articles belonging to Examples 1 - 2 were excellent in oxygen permeability, while the articles belonging to Controls 1 - 3 were inferior oxygen permeability.